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RESEARCH MEMORANDUM

COMPARISON OF COMBUSTION REACTIVITY OF ETHYLDECABORANE
FUELS WITH TYPICAL HYDROCARBON FUELS ON BASIS OF
SPRAY FLAMMABILITY LIMITS OF FUEL-RICH MISTS AND
CALCULATED LEAN-LIMIT FLAME TEMPERATURES
FOR FUEL VAPOR-AIR SYSTEMS

By Paul H. Wise and Abraham Lipschitz

Lewis Flight Propulsion Laboratory

Cleveland, Ohio

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NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS

RESEARCH MEMORANDUM

COMPARISON OF COMBUSTION REACTIVITY OF ETHYLDECABORANE FUELS WITH
TYPICAL HYDROCARBON FUELS ON BASIS OF SPRAY FLAMMABILITY LIMITS
OF FUEL-RICH MISTS AND CALCULATED LEAN-LIMIT FLAME
TEMPERATURES FOR FUEL VAPOR-AIR SYSTEMS

By Paul H. Wise and Abraham Lipschitz

SUMMARY

The spray flammability limits of various high-energy fuels and hydrocarbon fuels were determined experimentally in an apparatus which measured the minimum percent of oxygen by volume that would permit the ignition of a particular fuel. The fluids investigated were ethyldecaboranes, aliphatic hydrocarbons, olefins, aromatic hydrocarbons, and esters.

The spray flammability limits of the ethyldecaborane fuels range from 2 to 5 percent oxygen, whereas the hydrocarbon fuels have spray flammability limits from 12 to 17 percent oxygen. The ethyldecaborane fuels burned at lower fuel-flow rates than hydrocarbon fuels of comparable volatility.

Lean-limit flame temperatures were calculated for the ethyldecaborane fuels and decaborane, and the values are compared to the corresponding values for some hydrocarbons.

INTRODUCTION

The current interest in compounds containing boron, hydrogen, and carbon as aircraft fuels capable of providing greater operating range has led to extensive investigation of the combustion performance and physical properties of these fuels which are pertinent to their application in aircraft. Some combustion studies of these fuels are discussed in references 1 and 2. References 3 to 6 present physical and chemical properties such as thermal stability and mechanical shock stability of various boron-carbon-hydrogen fuels.

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This report describes an experimental investigation of the reactivity of these fuels with oxygen by measuring the minimum concentration of oxygen required in a fuel-oxygen-nitrogen mist to permit ignition of the fuel.

An apparatus and technique for measuring the minimum percent of oxygen required for ignition of a fuel mist are described in reference 7, and the minimum percent of oxygen thus determined, expressed as percent of oxygen by volume in the oxygen-nitrogen gas mixture, is defined as the spray flammability limit. This technique was applied to four samples of ethyldecaborane fuels and nine hydrocarbons of various types and volatilities, and the results are reported herein.

The lean-limit flame temperature (flame temperature for fuel vapor-air mixture at flash point) was calculated for the ethyldecaborane fuels and decaborane. The values are compared to the lean-limit flame temperature values for hydrocarbons (ref. 8) as a means of estimating the activation energy of the ethyldecaborane fuels in relation to the activation energy for hydrocarbon fuels in the combustion reaction.

FUELS AND APPARATUS

Fuels

The ethyldecaborane fuels were commercial samples supplied by the Bureau of Aeronautics, Department of the Navy, as part of Project Zip. The compositions and some properties of the ethyldecaborane fuels are presented in table I. The hydrocarbons (table I) were prepared and purified by the NACA or procured from the Bureau of Standards. The ethylacetate was a commercial sample.

Apparatus

The apparatus used in this project is similar to that described in reference 7. It consists of a horizontal combustion chamber (fig. 1) open at one end and fitted with a high-energy spark gap to ignite the fuel mist. The closed end of the combustion chamber supported a thermocouple to measure the temperature rise in the combustion chamber and the atomizing nozzle (fig. 2) for introducing the fuel mist. Oxygen and nitrogen were metered to a mixing chamber from which this oxidant-gas mixture flowed to the fuel atomizer (fig. 3) which introduced the fuel-oxygen-nitrogen mist to the combustion chamber. The oxidant-gas mixture was supplied to the atomizer at a pressure of 18 to 28 pounds per square inch gage with a total gas flow of 9 to 10 liters per minute at standard temperature and pressure. The fuel was metered to the atomizer by driving the plunger of a hypodermic syringe with a constant-speed electric

motor. Fuel-flow rates of 2.6, 4.7, or 15.0 milliliters per minute could be obtained by selecting the proper size syringe. The mist moved at about 5.7 to 5.8 centimeters per second in the combustion chamber.

Stainless steel was used for the combustion chamber because it was expected to withstand, better than brass, the combined corrosive effects of the solid products of combustion and the frequent washing to remove these products.

The ignition system was a combination of a high-voltage low-energy a-c spark operating at 120 sparks per second and a low-voltage high-energy continuous d-c spark (similar to ref. 9). A reasonable estimate for the rate of energy dissipation at the spark gap would be 300 joules per second.

PROCEDURE

The syringe was filled with the fuel to be tested. The wall temperature of the combustion chamber was brought to $24^{\circ} \pm 2.5^{\circ}$ C by the flow of water in the jacket, and the pressure regulators were adjusted at the oxygen and nitrogen cylinders to give the desired oxygen-nitrogen mixture. The gas was allowed to run through the chamber for about 45 seconds before the fuel flow was started. The fuel flow was initiated by starting the motor to drive the plunger of the syringe and opening the fuel needle valve of the atomizing nozzle to the full open position. Five seconds after commencing the operation of the atomizing nozzle, the arc was started and allowed to burn for about 5 seconds. An increase in temperature of about 15° to 20° C as indicated by the thermocouple was taken as a positive test for ignition. After the test, the chamber was thoroughly cleaned, and the electrodes were removed, cleaned, filed, and respaced.

RESULTS AND DISCUSSION

The spray flammability limits of several ethyldecaborane fuels were determined by measuring the minimum percent of oxygen required for ignition of flowing fuel-oxygen-nitrogen mists. The lean-limit flame temperatures for three samples of ethyldecaborane and for decaborane were calculated for the fuel-air mixture at the flash point of these fuels. The data and results are presented in tables II and III. Spray flammability limits are presented as a range, generally of 2 percent. This range represents the reproducibility of the experimental results.

Spray Flammability Limits

The spray flammability limits show a marked difference between the ethyldecaborane and the hydrocarbon fuels. At equivalent fuel-flow rates (2.6 ml/min) three ethyldecaborane fuels require only 2 to 5 percent oxygen for ignition, whereas eight hydrocarbons and ethylacetate require from 11 to as high as 17 percent oxygen.

Dodecane, which is comparable in volatility to the ethyldecaborane fuels, required not only more oxygen but also a much higher fuel-flow rate for ignition in this apparatus. Dodecane required 12 to 14 percent oxygen and a fuel flow of 15 milliliters per minute, more than 5 times the fuel flow for the ethyldecaborane fuels. Aliphatic normal hydrocarbons higher in molecular weight than n-nonane would not ignite and burn in this apparatus at fuel-flow rates of 2.6 or 4.7 milliliters per minute. In all of the positive tests for both hydrocarbon and ethyldecaborane fuels, combustion occurred in a fuel-rich condition.

One sample of ethyldecaborane fuel, 56Z2, failed to ignite in this system, although oxygen concentrations as high as 15 percent and fuel flows of 2.6 and 4.7 milliliters per minute were used. A possible explanation may be the higher viscosity of this sample and the resulting poorer spray distribution in comparison to the fuels which ignited successfully. The viscosities of the ethyldecaborane fuels are given in the following table:

Fuel	Kinematic viscosity at 25° C, centistokes
56Z2	13.9 (Unpublished data (Callery))
55Z1	6.1 (Unpublished data (Olin Mathieson))
55Z7	6.01 (Unpublished data (Olin Mathieson))
55Z8	6.4 (Unpublished data)

The viscosity of 56Z2 is twice that of the three other fuel samples. The high viscosity may have hindered the atomization of 56Z2 by the simple nozzle used in these experiments.

Comparisons of the flash points, spontaneous ignition temperatures, and spray flammability limits of the ethyldecaborane fuels as a class with the hydrocarbon fuels measured in this investigation reveal no trends other than the difference of the spray flammability limits. This difference indicates that the ethyldecaborane fuels are much more reactive in the combustion reaction than hydrocarbons.

Lean-Limit Flame Temperatures

The lean-limit flame temperatures for the ethyldecaborane fuels (55Z1, 55Z7, and 55Z8) and decaborane were calculated according to the

method of reference 10. The fuel vapor-air mixture, calculated from the vapor pressure of the fuels at the respective flash points (ref. 11), was used as the mixture composition for the lean-limit flame. The values of the lean-limit flame temperature are included in table III along with those for benzene and heptane from reference 8.

Reference 8 states that the activation energy of the rate-determining reaction in a lean-limit flame is proportional to the lean-limit flame temperature. The lean-limit flame temperature values for decaborane (696° K) and for the three samples of ethyldecaborane (725° , 790° , and 879° K) are roughly one-half the values for benzene (1715° K) and heptane (1980° K), which are typical of the values for 22 hydrocarbons in reference 8. It seems reasonable to assume that the activation energies of the ethyldecaborane fuels are also about one-half the activation energies of the hydrocarbons. A lower value of activation energy for the ethyldecaborane fuels agrees with the increased combustion reactivity and decreased spray flammability limit which have been found experimentally.

SUMMARY OF RESULTS

The experimental determination of the minimum percent of oxygen (expressed as volume percent of the oxidant-gas mixtures) required for ignition of flowing (5.7 to 5.8 cm/sec) fuel-oxygen-nitrogen mists, when a fixed amount of electrical energy is supplied in the form of a spark discharge in the mist, gave the following results:

1. Three samples of ethyldecaborane fuels required 2 to 5 percent oxygen by volume.
2. Eight hydrocarbons required 11 to 17 percent oxygen for the same fuel-flow rate as for the ethyldecaborane fuels.
3. Dodecane, which is comparable in volatility to the ethyldecaborane fuels, required a fuel-flow rate 5 times greater than the ethyldecaborane fuels as well as 12 to 14 percent oxygen for ignition.
4. One sample of ethyldecaborane fuel failed to ignite with oxygen concentrations as high as 15 percent and fuel flows somewhat higher than those used for the other ethyldecaborane fuels in this program.
5. Calculated lean-limit flame temperatures for the ethyldecaborane fuels are approximately one-half the values for hydrocarbon fuels which suggests that the combustion activation energies are also about one-half the activation energies of hydrocarbon fuels.

Lewis Flight Propulsion Laboratory
National Advisory Committee for Aeronautics
Cleveland, Ohio, December 12, 1956

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TABLE I. - COMPOSITION AND PROPERTIES OF FUELS

Fuel name or sample number	Composition	Boiling point at 760 mm Hg, °C	Flash point, °C	Spontaneous ignition temperature, °C
55Z1	Monoethyl- decaborane, 95 percent pure	^a 283	^b 59	^b 123
55Z7	Monoethyl- decaborane, 99 percent pure	^a 220	^b 73	^b 123
55Z8	2/3 Monoethyl- decaborane, 1/3 diethyldeca- borane	^a 242	^b 45	^b 130
56Z2	Mixed ethyl derivatives of decaborane and pentaborane	----	^c 65	^c 147
Benzene	98+ mole percent ↓ Commercial	^d 80.1	^e -11	^f 592
Toluene		^d 110.6	^e 10	^f 568
p-Xylene		^d 138.3	----	^f 565
n-Hexane		^d 68.7	^e -18	^f 261
n-Heptane		^d 98.4	^e -2	^f 247
n-Octane		^d 125.6	^e 13	^f 240
n-Nonane		^d 150.8	^b 33	^f 234
n-Dodecane		^g 215.9	^b 78	----
1-Hexene		^d 63.5	---	^f 272
Ethylacetate		^h 77	^h -4	^h 486

^aCalculated boiling point. Fuel decomposes below boiling point at 760 mm.

^bRef. 11.

^cUnpublished NACA data.

^dRef. 12.

^eRef. 13.

^fRef. 14.

^gRef. 15.

^hRef. 16.

TABLE II. - SPRAY FLAMMABILITY LIMITS OF FUELS

Fuel name or sample number	Fuel injection rate, ml/min	Fuel-oxygen ratio			Spray flammability limit, percent oxygen in gas stream
		Molar	Weight	Percent stoichiometric	
High-energy fuels					
55Z1	2.6	1.030	4.83	1445	2 - 4
55Z7	2.6	.782	3.66	1090	3 - 5
55Z8	2.6	.893	4.22	1260	3 - 4
56Z2	2.6				No ignition up to 15 percent oxygen
	4.7				
Other than high-energy fuels					
Benzene	2.6	0.500	1.22	375	14-16
	4.7	.714	1.74	535	>19
Toluene	2.6	.416	1.20	375	13-15
	4.7	.555	1.60	500	17-19
p-Xylene	2.6	.333	1.10	350	14-16
<u>n</u> -Hexane	2.6	.425	1.14	404	11-13
	4.7	.417	1.12	396	19
<u>n</u> -Heptane	2.6	.312	.976	343	14-15
	4.7	.476	1.49	523	16-18
<u>n</u> -Octane	2.6	.244	.868	305	15-17
<u>n</u> -Nonane	2.6	.270	1.08	379	12-14
	4.7	.444	1.78	623	13-15
<u>n</u> -Dodecane	15.0	1.150	6.10	2130	12-14
<u>l</u> -Hexene	2.6	.384	1.01	346	13-15
	4.7	.540	1.42	486	17-19
Ethylacetate	2.6	.588	1.62	295	11-12
	4.7	.769	2.11	385	15-17

TABLE III. - LEAN-LIMIT FLAME TEMPERATURES
CALCULATED FOR COMPOSITION AT FLASH POINT

Fuel	Flash point, °C	Vapor pressure at flash point, mm Hg	Fuel-air ratio		Lean-limit flame temperature, °K
			Weight	Percent stoichiometric	
Benzene	^a -11	^b 10.45	-----	-----	^c 1715
n-Heptane	^a -2	^b 10.02	-----	-----	^c 1980
Decaborane	^d 50	^e 1.19	0.00558	6.96	696
55Z1	^d 59	^f 1.19	.00666	8.60	725
55Z7	^d 73	^f 1.73	.00936	12.09	879
55Z8	^d 45	^g 1.43	.00841	10.95	790

^aRef. 13.

^bCalculated from vapor-pressure - temperature equations in ref. 12.

^cRef. 8.

^dRef. 11.

^eCalculated from vapor-pressure - temperature equation in ref. 17.

^fCalculated from vapor-pressure - temperature equations available as unpublished data.

^gUnpublished data.

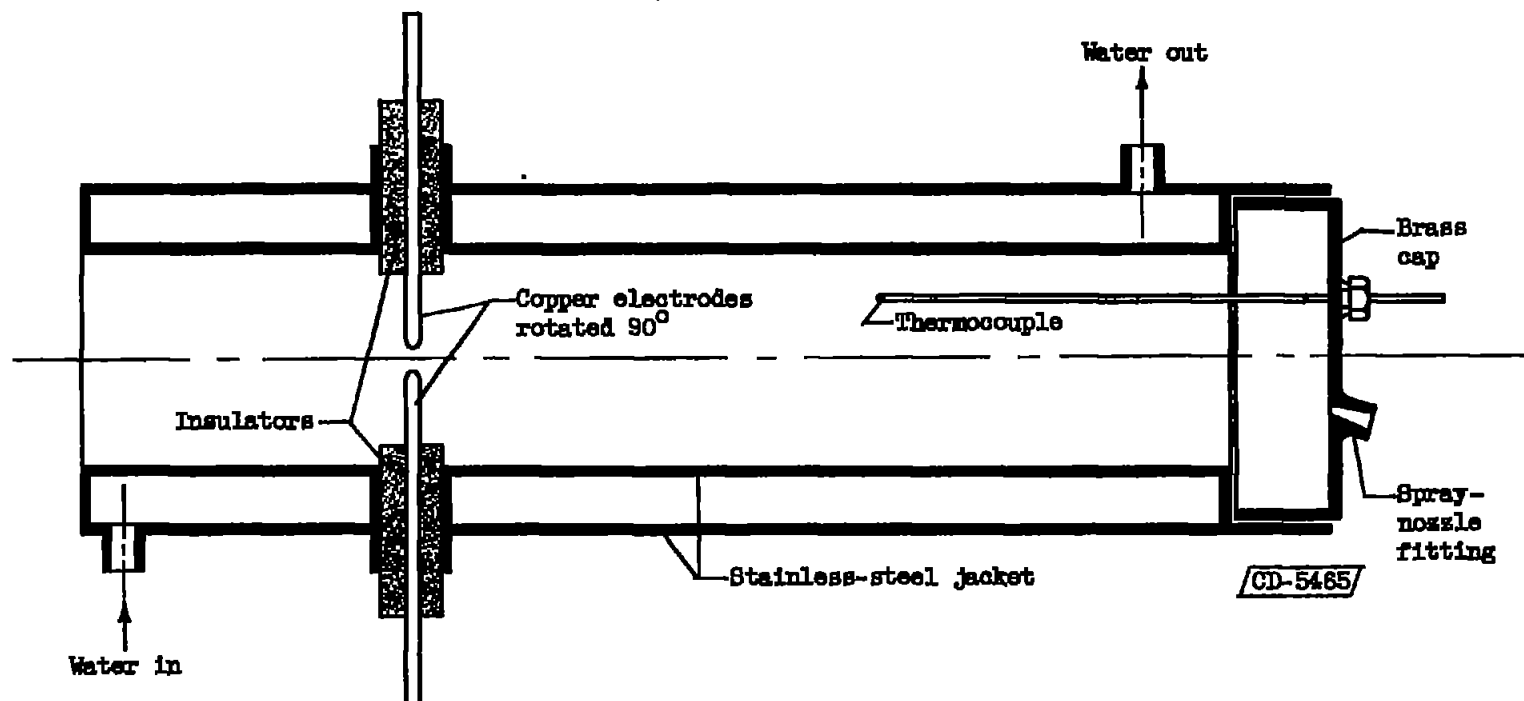


Figure 1. - Combustion chamber.

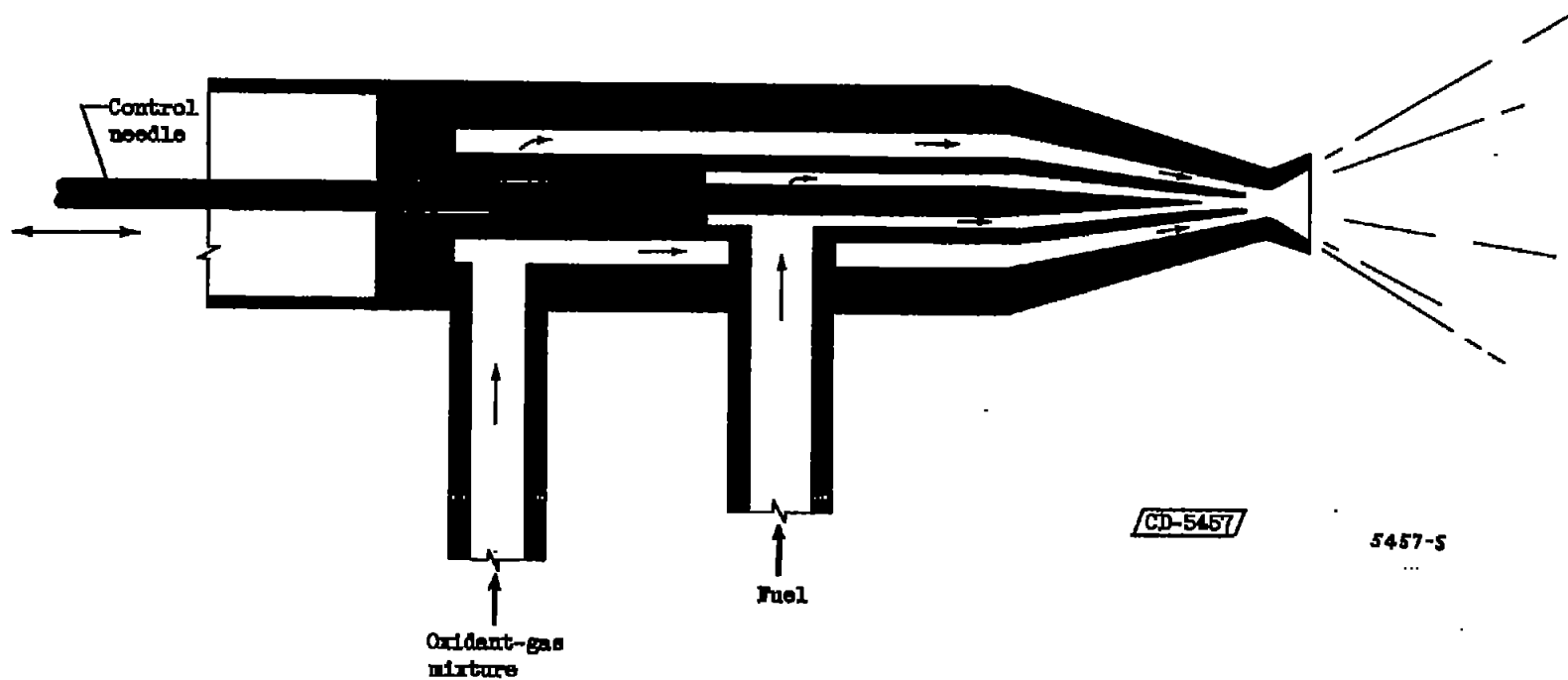


Figure 2. - Atomizing nozzle.

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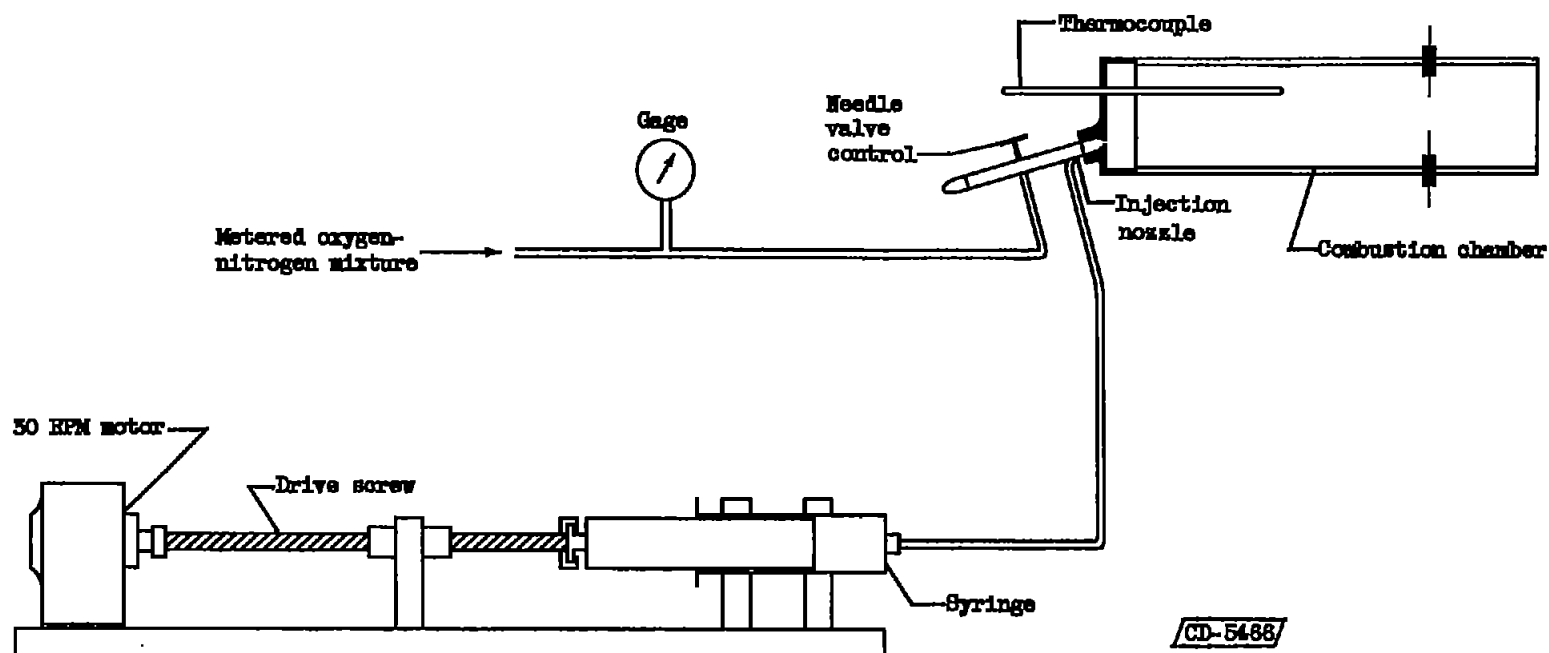


Figure 3. - Fuel metering and atomizing system with combustion chamber.